



## Analytical note

## Analytical capabilities of Energy Dispersive X-Ray Fluorescence for the direct quantification of iron in cocoa powder and powdered cocoa drink

D. Andrey<sup>a</sup>, J.P. Dufrier<sup>b</sup>, L. Perring<sup>a,\*</sup><sup>a</sup> Analytical Science - Rapid Methods Group, Nestlé Research Centre, Vers chez-les-Blanc, CH-1000 Lausanne 26, Switzerland<sup>b</sup> Quality Management, Nestlé Research Orbe, Route de Chavornay 3, CH-1350 Orbe, Switzerland

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## ABSTRACT

The objective of this study was to develop and validate a quick and easy method for the quantification of iron by Energy Dispersive X-Ray Fluorescence (ED-XRF) in cocoa powder and powdered cocoa drink. Pellets of 6 g were prepared under 10 tons. Total time to analyze both sides of pelletized samples is 150 s. During this validation step, the iron concentrations obtained by ED-XRF were systematically evaluated against those obtained from inductively coupled plasma-atomic emission spectrometry. This feasibility study demonstrates the good potential of ED-XRF technique as an accurate, simple, cheap and rapid method. Indeed, ED-XRF method was found to be comparable to the reference one; furthermore, the bias between both methods was found to be not significantly different from 0. Robust relative repeatabilities and intermediate reproducibilities were found to be lower than 1.5%. The expanded uncertainties represent less than 12% of the median concentration of the validation samples.

## 1. Introduction

X-Ray Fluorescence (XRF) has been established over the last decades as an efficient technique for accurate and non-destructive elemental analysis in miscellaneous environments such as on-field, R&D and factory laboratories or close to production lines in control rooms [1, 2]. This analytical technique covers numerous applications including those of agriculture and food industry. For illustration purpose, a non-exhaustive list of food matrices analyzed by X-Ray Fluorescence is given in Table 1.

Contrary to various official methods based on atomic absorption spectrophotometry (AAS) and inductively coupled plasma - atomic emission spectrometry (ICP-AES), the energy dispersive (ED)-XRF technique is not destructive. It allows the direct measurement with a minimum of sample treatment meaning that measurements can be carried out directly on powdered samples (into pellet form or poured in cup) [21]. Therefore it avoids time-consuming preparation steps, usage of acidic and corrosive reagents needed for sample digestion and the generation of waste (consistent with “green” chemistry principles) and expensive equipment operated by qualified technicians in restrictive laboratory safe environments.

This technique generating reliable and timely results during the manufacturing, it can be easily implemented in factory labs or control rooms owing to its simplicity of use, to rapidly adapt and optimize

process parameters [22] and finally check the quality and compliance of resulting processed products.

In the present study, the ED-XRF technique is currently proposed as an interesting alternative to classical reference technique(s) for content control of iron in cocoa powders and powdered cocoa drinks. Indeed, regulatory tolerances are becoming tighter for fortified processed products, leading to higher risk of noncompliant products. In the case of powdered cocoa drinks, the impact of variation of iron content in cocoa powder in the finished beverage is higher than the tolerances allowed to the finished product. Our cocoa powder monitoring values for Iron in cocoa powders were found from 10 to 120 mg/100 g (Fig. S1).

In the context and in order to ensure compliance, both raw materials (cocoa powder) and finished products (powdered cocoa drink) need to be controlled for routine quality management. Rapid and accurate measurements must therefore be implemented in the factories producing these beverages. Using such analytical technique can allow more systematic controls as well as avoiding the shipment of numerous samples to external/centralized laboratories for reference method analyses, and consequently contributes to the reduction of the working capital on production sites.

\* Corresponding author.

E-mail address: [loic.perring@rdls.nestle.com](mailto:loic.perring@rdls.nestle.com) (L. Perring).

**Table 1**  
Non exhaustive list of food matrices analyzed by X-Ray Fluorescence.

Matrix	XRF type	Investigated analytes	Sample denomination	Year	References
Premixes/mineral supplements	WD-XRF	P and Ca	Mineral supplements for cattle	2018	[3]
	ED-XRF	Fe, Cu and Zn	Mineral premixes	2005	[4]
Non processed cereals	ED-XRF	Fe, Zn and Se	Whole grain wheat	2012	[5]
	T-XRF	P and S	Rice (white and brown)	2012	[6]
Processed cereals	WD-XRF	Na, Mg, P, Cl, K, Ca, Mn, Fe and Zn	Infant cereals	2005	[7]
	ED-XRF	Fe	Infant cereals	2007	[8]
	ED-XRF	Na, Mg, P, Cl, K, Ca, Fe	French bread	2015	[9]
Milk-based powders	ED-XRF	P, S, Cl, K, Ca, Fe, Zn	Milk-based products	2003	[10]
	WD-XRF	Na, Mg, P, S, Cl, K, Ca, Fe and Zn	Milk-based products	2004	[11]
	WD-XRF	Al, Cu, Fe and Zn	Infant milk powders	2015	[12]
Yoghurt/cheese	WD-XRF	P, K, Ca, Fe and Zn	Yoghurt, ultra filtered milk	2009	[13]
	ED-XRF	Na	Cheese	2015	[14]
Dehydrated bouillons	ED-XRF	Na, Mg, P, Cl, K, Ca, Fe and Zn	Dehydrated bouillon, sauce based powders	2017	[15]
Tea/coffee	ED-XRF	Ti, Cr, Mn, Fe, Co, Ni, Cu and Zn	Black tea	2008	[16]
	ED-XRF	P, S, Cl, K, Ca, Mn, Fe, Cu, Zn, Br, Rb, and Sr	Ground coffee	2017	[17]
Confectionery	T-XRF	Ti, Cr, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr, and Pb	Candies	2010	[18]
Dry pet food	ED-XRF	Na, Mg, P, Cl, K, Ca, Mn, Fe, Cu and Zn	Dry pet food	2016	[19]
	ED-XRF	Zn	Dry feeds for cats and dogs	2016	[20]

## 2. Materials and methods

### 2.1. Calibration and validation samples

One set of 29 cocoa powders (CP) and one set of 30 powdered cocoa drinks (PCD) were provided by one production site. Cocoa powders were used as received from suppliers. Samples of finished products (powdered cocoa drink) were obtained by spiking one recipe with iron at different levels, variable amounts of Iron Pyrophosphate were therefore added to obtain and cover wide enough ranges of concentrations.

All the samples of PCD were homogenized by using a kitchen appliance Thermomix® from Vorwerk. The efficiency of the mixing was checked by performing repeatability measurements on ED-XRF on sample powders pelletized several times. As soon as the homogeneity was under control, the reference method and ED-XRF analyses were initiated. The final results of relative standard deviations of robust repeatability  $CV_{rob}(r)$  described in paragraph 3.6 are found similar between CP and PCD powders.

Their iron concentrations of all the samples (Table S1) were obtained by reference method and were used afterwards to calibrate ED-XRF instrument and validate the method.

### 2.2. Reference method

Reference values of all samples were determined for iron according to the official method from AOAC [23]. This method is currently used to simultaneously determine nine nutritional elements (Na, Mg, P, K, Ca, Mn, Cu, Fe and Zn) in food products by inductively coupled plasma - atomic emission spectrometry (ICP-AES). Sample digestion is performed through acidic wet digestion of food samples by microwave technology with either closed- or open-vessels.

All analyses were done in single.

### 2.3. Energy Dispersive X-Ray Fluorescence method

#### 2.3.1. Sample preparation

Portions of  $6.0 \pm 0.1$  g of homogenized powder were pelletized using a die set made of hardened stainless steel in order to prepare 32 mm diameter pellets. No binder was found needed as an aid for pelletizing.

Using a benchtop electro hydraulic press (max. 20 ton load) (LGC Standards, United Kingdom) and related accessories (Specac, United Kingdom), the pressure was set at 10 tons. After pelletizing and between analyses, all pellets were stored in a desiccator. Between each sample,

the pelletizing die and the sample holder were washed thoroughly with soapy water, and then rinsed with ethanol before drying.

Only one pellet was prepared per sample. Indeed, the information depth from a sample depends on the energy of the element of interest and varies from around 1  $\mu$ m for Mg up to around 2 mm for Zn in such type of food application. Therefore, as the prepared pellets present a thickness greater than 5 mm, they can be considered as infinite thick. Thus, pellets analyzed on both sides were considered as real duplicates. Internal checks between pellets analyzed on both sides versus pellets analyzed in duplicates demonstrated similar performances.

#### 2.3.2. Instrumental conditions

For this study, an ED-XRF Epsilon 3XLE from PANalytical (Almelo-Netherlands) equipped with an Ag anode tube (maximum voltage = 50 kV) was used to acquire the XRF spectra. The system was equipped with a 10-position sample holder allowing sample spinning during measurement. By rotating the pellets during the analyses, it reduces potential errors introduced by sample preparation and heterogeneity.

Previous conditions developed for other foodstuffs [15, 20] on the same instrument, were adapted; accelerating voltage and current were optimized in order to get the best balance of sensitivity for the investigated element regarding peak heights and the ratios “peak to background”. Measurements were done under air. The instrumental conditions are shown in Table 2. The collection of ED-XRF spectra, spectra fitting, integration of peak and region of interest (ROI) areas and the calculation of models were done using the Epsilon 3 software from PANalytical.

The intensity of iron X-Ray Fluorescence peaks does not depend on its concentration only, but also on the total matrix composition (Compton's effect). In order to reduce matrix effect (linked to raw materials variation and its organic content) and to compensate it, the fluorescence peak was normalized using an spectrum area (see

**Table 2**  
ED-XRF instrumental condition, with details of ED-XRF signal integration.

ED-XRF parameters	
X-ray tube	Ag
Voltage (kV)	15
Current ( $\mu$ A)	1000
Filter	Al foil 200 $\mu$ m
Atmosphere	Air
Analyte line (keV)	Fe-K $\alpha$ (6.4)
Normalizing background (keV)	from 11.0 to 12.0
Measuring time (s)	60

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